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(54)【発明の名称】 リチウム二次電池

(57)【特許請求の範囲】

【請求項1】リチウム二次電池において、式(I)

$Li_{(Co_{1-y}Ni_y)}O_2$ (I)

(式中、yは $0.75 < y \leq 0.9$ である)で示される状態に共沈法により合成されたリチウム(コバルトニッケル)酸化物から充電によりリチウムの一部を抜いた式(II)

$Li_x(Co_{1-y}Ni_y)O_2$ (II)

(式中、xは $0 < x < 1$ で、yは $0.75 < y \leq 0.9$ である)で示されるリチウム(コバルトニッケル)酸化物を正極活物質として用いたことを特徴とするリチウム二次電池。

【発明の詳細な説明】

【産業上の利用分野】

本発明は、リチウム二次電池に係わり、さらに詳しく

はその正極活物質の改良に関する。

【従来の技術】

従来、リチウム二次電池用の正極活物質としては、二硫化チタン、二硫化モリブデンなどの金属硫化物が使用されていた。

しかし、これらの金属硫化物系正極活物質は、電池電圧が3V以下で、エネルギー密度の高い電池を得る観点からは、電池電圧が低いという問題があった。

そこで、よりエネルギー密度が高い電池を得るために、 $LiCoO_2$ を正極活物質として用いることが検討されている(例えば、米国特許4,567,031号明細書)。

この $LiCoO_2$ を二次電池に用いた場合の充放電サイクルと容量の劣化の関係はいまだ報告されていないが、 $LiCoO_2$ を正極活物質として用いた場合、電圧が4.5~3.9Vと高いため、電解液の分解(正確には電解液の溶媒として

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CLAIMS

(57) [Claim(s)]

[Claim 1] It sets to a lithium secondary battery and is a formula (I).

$\text{Li}(\text{Co}_{1-y}\text{Ni}_y)\text{O}_2$ (I)

It is the formula (II) which extracted some lithiums by charge from the lithium (cobalt-nickel) oxide compounded with the coprecipitation method by the condition by which it is shown by (the inside of a formula and y are $0.75 < y \leq 0.9$).

$\text{Li}_{x}(\text{Co}_{1-y}\text{Ni}_y)\text{O}_2$ (II)

It is the lithium secondary battery characterized by using the lithium (cobalt-nickel) oxide shown by (x are $0 < x < 1$ among a formula, and y is $0.75 < y \leq 0.9$) as positive active material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]

This invention relates to amelioration of the positive active material in more detail with respect to a lithium secondary battery.

[Description of the Prior Art]

Conventionally, as positive active material for lithium secondary batteries, metallic sulfide, such as 2 titanium sulfides and molybdenum disulfide, was used.

However, cell voltage was less than [3V], and such metallic sulfide system positive active material says [it] that cell voltage is low and had it from a viewpoint which obtains a cell with high energy density. [problematic]

Then, in order to obtain a cell with more high energy density, using LiCoO_2 as positive active material is examined (for example, U.S. Pat. No. 4,567,031 number specification).

Although the charge-and-discharge cycle at the time of using this LiCoO_2 for a rechargeable battery and the relation of degradation of capacity are not yet reported, when LiCoO_2 is used as positive active material, since the electrical potential difference is as high as 4.5-3.9V, it is thought that disassembly (decomposition by oxidation reaction and polymer-izing of the organic solvent correctly used as a solvent of the electrolytic solution) of the electrolytic solution arises.

In the organic solvent used as an electrolytic-solution solvent, even propylene carbonate excellent in oxidation resistance oxidizes from the 4.2V - 4.5V neighborhood to a lithium pole in 25 degrees C of platinum best quality, it is begun to decompose it, and carbon dioxide gas (CO_2) is generated [others [1443 / (1986) / G.Eggert et al., *Electrochimica Acta.*, 31 (11), and]].

Moreover, there is much what also disassembles a polymer electrolyte from the 4V neighborhood.

Therefore, in order to use the organic system electrolytic solution known now, it is desirable to limit the upper limit of cell voltage to the 4V neighborhood, when preventing disassembly of the electrolytic solution.

Then, when this invention persons did the charge and discharge of the lithium secondary battery which used LiCF_3O_2 as positive active material in [electrical-potential-difference] not more than 4V, it became clear that the charge-and-discharge capacity

which can be used is small.

[Problem(s) to be Solved by the Invention]

When the charge and discharge of this invention are carried out in [electrical-potential-difference] not more than 4V from a viewpoint in which the lithium secondary battery which used for positive active material LiCoO₂ expected as a high energy consistency cell prevents disassembly of the electrolytic solution, it solves the trouble that the charge-and-discharge capacity which can be used is small, and aims at offering the lithium secondary battery which can obtain a big charge-and-discharge capacity also in the charge and discharge in the electrical-potential-difference range which can prevent disassembly of the electrolytic solution.

[The means for solving a technical problem]

When this invention makes nickel dissolve to LiCoO₂, open circuit voltage is reduced and charge-and-discharge capacity also with the big charge and discharge of the electrical-potential-difference range not more than 4V is obtained.

That is, this invention is a formula (I) as positive active material.



It is the formula (II) which extracted some lithiums by charge from the lithium (cobalt-nickel) oxide compounded with the coprecipitation method by the condition by which it is shown by (the inside of a formula and y are $0.75 < y \leq 0.9$).



It is related with the lithium secondary battery characterized by using the lithium (cobalt-nickel) oxide shown by (x are $0 < x < 1$ among a formula, and y is $0.75 < y \leq 0.9$).

By using the lithium (cobalt-nickel) oxide shown by the above formulas (II), open circuit voltage falls and the reason a big charge-and-discharge capacity comes to be obtained in [electrical-potential-difference] not more than 4V is considered as follows.

The range of the open circuit voltage of the lithium secondary battery which used LixCoO₂ for positive active material is 4.6-3.9V. That is, it follows on x changing between 0-1, and changes in the range whose open circuit voltage is 4.6-3.9V. And the range of the amount of Li(s) included in the electrical-potential-difference range not more than 4V has only $0.7 \leq x \leq 1$. And in the range in which x approaches 1, since polarization cannot use greatly, the actually available range becomes still narrower.

Therefore, Li can change only in the very narrow range, but since the range which can be used for charge and discharge is very narrow, the charge-and-discharge capacity obtained becomes small.

On the other hand, in the lithium secondary battery which used Lix(Co_{1-y}Ni_y) O₂ for positive active material, open circuit voltage is the range which is 4V a little more than -3.5V (it follows on x changing between 0-1 like the above, and changes in the range whose open circuit voltage is 4V a little more than -3.5V). And although the field (that is, the range of the amount of Li(s)) of x included in the electrical-potential-difference range not more than 4V changes with amounts of dissolution of nickel (that is, y value), in the case of y= 0.8, it becomes the range of $0.45 \leq x \leq 1$, and the range where x may change from the case of LixCoO₂ becomes large. Therefore, the range which can carry out charge and discharge in [electrical-potential-difference] not more than 4V becomes large, and the charge-and-discharge capacity obtained becomes large.

In Lix(Co_{1-y}Ni_y) O₂ of the formula (II) showing the lithium (cobalt-nickel) oxide used as positive active material in this invention Making y into the range of $0.75 < y \leq 0.9$

Polarization will become large if y exceeds 0.9 (if it is got blocked and the amount of dissolution of nickel increases). When it is because charge-and-discharge capacity falls and y becomes small too much, (when it is got blocked and the amount of dissolution of nickel decreases) Since there are few amounts of dissolution of nickel, It is because the fall of open circuit voltage decreases, the range from which x can change in [electrical-potential-difference] not more than 4V becomes narrow and the charge-and-discharge capacity obtained becomes small.

The lithium (cobalt-nickel) oxide shown by the above-mentioned formula (II) used as positive active material in this invention is obtained based on compounding the lithium (cobalt-nickel) oxide shown by the formula (I) with a coprecipitation method. That is, even when are based on a coprecipitation method, and y in a formula (I) and a formula (II) is a high value of $0.75 < y \leq 0.9$, a lithium (cobalt-nickel) oxide with a large charge-and-discharge capacity is obtained, but if y becomes high to about $0.75 < y \leq 0.9$ when based on alligation, a lithium (cobalt-nickel) oxide with a large charge-and-discharge capacity will no longer be obtained.

In this invention, the coprecipitation method which obtains the above-mentioned lithium (cobalt-nickel) oxide means how to compound lithium (cobalt-nickel) oxide through the process which is made to carry out coprecipitation of Co (cobalt) and the nickel (nickel) as a carbonate out of the water solution containing Co ion and nickel ion, and is used as uniform mixture.

In the cell of this invention, although a lithium or a lithium alloy is used for a negative electrode, as a lithium alloy used for such an application, a lithium-aluminium alloy, a lithium-tin alloy, a lithium-zinc alloy, a lithium-lead alloy, a lithium-bismuth alloy, a lithium-silicon alloy, a lithium-regulus metal, a lithium-Magnesium alloy, a lithium-indium alloy, a lithium-gallium alloy, a lithium-germanium alloy, a lithium-gallium-indium alloy, etc. are raised, for example. Moreover, what carried out little addition can use the metal of further others for those lithium alloys at a negative electrode.

Especially the thing by which the electrolytic solution is also usually used for this kind of cell can be used as it is, without receiving constraint. When the electrolytic solution is illustrated, for example 1, 2-dimethoxyethane, ethylene carbonate, Propylene carbonate, gamma-butyrolactone, a tetrahydrofuran, To independent or two or more sorts of mixed solvents of organic solvents, such as 1, 3-dioxolane, the 4-methyl -1, and 3-dioxolane For example, what was prepared by dissolving one sort of electrolytes, such as LiClO₄, LiPF₆, LiAsF₆, LiSbF₆, LiBF₄, and LiB (C₆H₅)₄, or two sorts or more is raised.

[Example]

Next an example is given and this invention is further explained to a detail.

Example 1 Li(Co_{1-y}Ni_y) O₂ were compounded. y is 0.8. When this is displayed according to a formula (I), it is Li(Co0.2nickel0.8) O₂.

Composition was performed as shown below. First, coprecipitation of Co (cobalt) and the nickel (nickel) was carried out as a carbonate (under the usual conditions, it becomes a basic carbonate) out of the water solution containing Co ion and nickel ion, and it considered as uniform mixture. This coprecipitation method is explained in detail later. After drying at 140 degrees C among [after rinsing the precipitate obtained as mentioned above] an argon, mixed with Li₂CO₃, and heat for 3 hours, it was made to react at 920 degrees C among air (N₂/O₂=80/20), and Li(Co0.2nickel0.8) O₂ were obtained by carrying out air quenching (how to take out and quench the heated sample in the

atmospheric air of ordinary temperature).

Coprecipitation out of the water solution containing Co ion and nickel ion of Above Co and nickel was performed as follows.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are dissolved in the pure water saturated in carbon dioxide gas so that the rate of nickel and Co may be set to 80:20 [nickel/Co=80 / 20 (mole ratio)] by the mole ratio, and NaHCO_3 water solution was added to this solution, and leaves and carried out coprecipitation to it.

After having added the scaphocerite-like graphite to this at 10% of the weight of a rate as an electronic conduction assistant, adding polytetrafluoroethylene at 5% of the weight of a rate as a binder and mixing using $\text{Li}(\text{Co0.2nickel0.8})\text{O}_2$ compounded as mentioned above, pressing was carried out by 3 t/cm², and the disc-like Plastic solid with a diameter [of 9mm] and a thickness of about 0.3mm was produced. The cell (model cel) shown in Fig. 1 , using the acquired Plastic solid as a positive electrode was produced.

In Fig. 1 , the A section expands only the important section of the above-mentioned cell, and does not show it, and after adding the flaky graphite with which one does not take a negative electrode among drawing and this negative electrode 1 does not take 2OLi0.1V5 powder 10% of the weight, and 5% of the weight of polytetrafluoroethylene and mixing, pressing is carried out, and it produces and consists of a disc-like Plastic solid with a diameter [of 16mm], and a thickness of about 2mm. And in a hexane, Li0.1V2O5 used as a negative-electrode active material make n-butyl lithium ($n\text{-C4H9Li}$) react to V2O5 , and they are compounded. 2 is a positive electrode, and this positive electrode 2 uses as positive active material $\text{Lix}(\text{Co0.2nickel0.8})\text{O}_2$ (however, x in a formula is $0 < x < 1$) which extracted some lithiums by charge from $\text{Li}(\text{Co0.2nickel0.8})\text{O}_2$ which are the above, and were made and compounded, and consists of a pressing object which added a scaphocerite-like graphite and polytetrafluoroethylene.

3 is the electrolytic solution which comes to carry out 1 mol/l dissolution of LiBF_4 at the mixed solvent of the capacity factor 2:1 of propylene carbonate and 1 and 2-dimethoxyethane, and 4 is a separator which consists of a polypropylene nonwoven fabric. 5 is a RIFERENSU pole which consists of a pressing object which uses Li0.1V2O5 as an active material, 6 is a container made from polypropylene, and 7 is a charge collector which consists of a platinum expanded network which carried out spot welding of the lead wire of platinum.

And theoretical quantity of electricity of the positive electrode of this cell sets a charge-and-discharge field to $\text{Lix}(\text{Co1-yNiy})\text{O}_2$ ($0 < x < 1$), and by setting a charge-and-discharge field to LixV2O5 ($0 < x \leq 1$), less than 15 mAh(s) and theoretical quantity of electricity of a negative electrode are 70mAh(s), and they are set up so that the direction of quantity of electricity of a negative electrode may become superfluous from quantity of electricity of a positive electrode.

Example 2 The value of y of $\text{Li}(\text{Co1-yNiy})\text{O}_2$ was compounded with the coprecipitation method to 0.9, $\text{Lix}(\text{Co0.1nickel0.9})\text{O}_2$ (however, x in a formula is $0 < x < 1$) which extracted some lithiums by charge from these $\text{Li}(\text{Co0.1nickel0.9})\text{O}_2$ was used as positive active material, and also the cell was produced like the example 1.

Example 1 of a comparison 0 [2], i.e., LiCoO_2 , was compounded for the value of y of $\text{Li}(\text{Co1-yNiy})\text{O}_2$, extracted some lithiums by charge from this LiCoO_2 , and LixCoO_2 (however, x in a formula is $0 < x < 1$) was used as positive active material, and also the cell was produced like the example 1.

Example 2 of a comparison The value of y of $\text{Li}(\text{Co}_{1-y}\text{Ni}_y)\text{O}_2$ was compounded with the coprecipitation method to 0.4, extracted some lithiums by charge from these $\text{Li}(\text{Co}_{0.6}\text{nickel}0.4)\text{O}_2$, and $\text{Li}_x(\text{Co}_{0.6}\text{nickel}0.4)\text{O}_2$ (however, x in a formula is $0 < x < 1$) was used as positive active material, and also the cell was produced like the example 1. Example 3 of a comparison The thing 2 of 1.0, i.e., LiNiO_2 , was compounded for the value of y of $\text{Li}(\text{Co}_{1-y}\text{Ni}_y)\text{O}_2$, and extracted some lithiums by charge from this LiNiO_2 , and Li_xNiO_2 (however, x in a formula is $0 < x < 1$) was used as positive active material, and also the cell was produced like the example 1.

Next, the charge and discharge of the cell of the above-mentioned examples 1-2 and the cell of the examples 1-3 of a comparison were performed. Charge and discharge performed the charging current and the discharge current in the electrical-potential-difference range between +0.6V--0.2V to the reference pole by 0.636mA (per unit cross section of a positive electrode 1.0 mA/cm²). Since $\text{Li}_{0.1}\text{V}_2\text{O}_5$ of a reference pole have the electrical potential difference of 3.4V to Li, this electrical-potential-difference range turns into the range of 4.0V-3.2V, when Li is used as a negative electrode.

The charge-and-discharge capacity in the above-mentioned electrical-potential-difference range of the cell of the above-mentioned examples 1-2 and the cell of the examples 1-3 of a comparison is shown in the 1st table. However, this charge-and-discharge capacity is the value of 3 cycle eye from which charge and discharge are stabilized and capacity serves as about 1 constant value. By this 3 cycle eye, charge capacity and discharge capacity become an almost equal value. In addition, in Fig. 1, in order to clarify change of the charge-and-discharge capacity accompanying change of the amount of nickel, it arranges in order of the amount of nickel (that is, value of y), and is displaying.

Therefore, the display order is different sequence from the above mentioned written sequence of an example or the example of a comparison.

第 1 表

電池	$\text{Li}_x(\text{Co}_{1-y}\text{Ni}_y)\text{O}_2$		3サイクル 目の充放電 容量(mAh)
	yの値	Ni/Co比(モル比)	
比較例 1	0	0/100	1.0
比較例 2	0.4	40/60	1.3
実施例 1	0.8	80/20	2.8
実施例 2	0.9	90/10	2.0
比較例 3	1.0	100/0	0.5

As shown in the 1st table, the cell of examples 1-2 using the positive active material which made nickel dissolve has a large charge-and-discharge capacity in the electrical-potential-difference range of 4.0-3.2V compared with the cell of the example 1 of a comparison using LiCoO_2 which is not making nickel dissolve as positive active material. It is because the field [that is, the field which a lithium ion (Li^+) can frequent] of this from which open circuit voltage falls and x changes with dissolution-ization of nickel in [electrical-potential-difference] not more than 4V increased. However, if the amount of dissolution of nickel (that is, y value) increases too much, charge-and-discharge capacity will fall with the increment in the amount of nickel. If the amount of

nickel increases too much, polarization will increase, and this is considered to be for capacity to fall.

In addition, although the capacity at the time of a charge-and-discharge cycle is investigated and the trial by the model cel was performed in the above-mentioned example, this is because the effect of cell configuration members other than positive active material, such as a negative electrode, appears and the difference in the charge-and-discharge cycle capacity by difference of positive active material stops being able to appear easily correctly by the mounting cell. Moreover, although LixV2O5 is used without using a lithium for a negative electrode In the case of a lithium, are easy to react with oxygen and moisture, and, as for this, a front face changes to Li2O, LiOH, etc.

Although a cell property tends to be influenced with a Li2O coat, a LiOH coat, etc. which are formed in this lithium front face, in LixV2O5, it is rare to such be influenced, and is because the difference in the cell property by difference of positive active material can grasp correctly.

And although the lithium (cobalt-nickel) oxide used as positive active material was expressed as Lix(Co1-yNiy)O2 in this invention, there is what a transition-metals part (part of CoNi) shifts in **5% of range a little from the stoichiometry in the above-mentioned formula. Moreover, oxygen may shift according to an oxygen defect etc., and since they do not almost affect a cell property, they are also contained under the category of this invention.

Moreover, although what dissolved LiBF4 in the mixed solvent of propylene carbonate and 1 and 2-dimethoxyethane as the electrolytic solution was used in the example, it may replace with it and other electrolytic solutions, for example, the electrolytic solution which dissolved LiBF4 in propylene carbonate, may be used.

[Effect of the Invention]

The formula which made nickel of the amount of specification dissolve to LiCoO2 in this invention as explained above (I)



It is the formula (II) which extracted some lithiums by charge from the lithium (cobalt-nickel) oxide compounded with the coprecipitation method by the condition by which it is shown by (the inside of a formula and y are $0.75 < y \leq 0.9$).



Charge-and-discharge capacity was able to be raised in [in which the stability of the electrolytic solution can secure LiCoO2 compared with the case where it uses as positive active material / electrical-potential-difference] not more than 4V by using the lithium (cobalt-nickel) oxide shown by (x are $0 < x < 1$ among a formula, and there is y $0.75 < y \leq 0.9$) as positive active material.

Drawing 1

